0.1 A Theory for Spin Glass Phenomena in Interacting Nanoparticle Systems

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Dilute magnetic nanoparticle systems exhibit slow dynamics [1] due to a broad distribution of relaxation times that can be traced to a correspondingly broad distribution of particle sizes [1]. However, at higher concentrations inter-particle interactions lead to a slow dynamics that is qualitatively indistinguishable from that dislayed by atomic spin glasses. A theory is derived below that accounts quantitatively for the spin-glass behaviour. The theory predicts that if the interactions become too strong the spin glass behaviour disappears. This conclusion is in agreement with preliminary experimental results.

At high temperatures assemblies of nanoparticles are superparamagnetic, but on cooling it has been shown [2] that they enter a spin glass phase. Dc magnetic relaxation has revealed ageing effects [3], and similar results have been obtained for the relaxation of the low-frequency ac susceptibility [4]. While ageing phenomena are certainly characteristic of spin glasses they are also displayed by many random systems, what possibly sets spin glasses apart is a dynamic memory effect that has been referred to as rejuvenation [5,6,7]: if the cooling in zero field is halted the susceptibility slowly decays. On resuming the cooling the susceptibility recovers to the value it would have had if the cooling had not been interrupted. On subsequent heating a decreased susceptiblity is observed in the vicinity of the temperature at which the cooling was halted. These effects have been observed in interacting nanoparticle systems [8,9,10,11]

The most elementary theory for magnetic interactions is a mean field theory; so in this spirit, the model that will be studied considers that a local interaction field is produced by the local magnetization that affects the local susceptibility. Because of the disorder, the local magnetization is spatially restricted, but the correlation length of the local field at low temperatures can be expected to be much larger than the average particle separation. At high temperatures all the particles are able to achieve their equilibrium distribution, but as the material is cooled the relaxation times increase, and eventually when the relaxation time of a particle becomes so long that it is unable to relax in the time remaining in the cooling process it becomes blocked. After cooling in zero field the magnetization of the sample must be zero. If a small field is applied and the sample slowly heated from a temperature that is low enough for all the particles to be

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blocked, some of the blocked grains will be remagnetized, and the sample will begin to acquire a moment. Initially the smallest particles with the shortest relaxation times are remagnetized followed by the larger particles as the temperature increases. The particle size distribution for these materials displays a broad peak, and is often well approximated by a log-normal distribution; so the number and size of remagnetized particles increases rapidly with temperature. The net magnetization is the result not only of the preferential orientation of the particle moment imposed by the field, but also the preferential growth of the correlation length for the local magnetization. The first is much larger than the second; so the increase in correlation length will be neglected.

If the cooling is interrupted, and the sample held at an intermediate temperature, T_w for a time t_w, some of the blocked particles, whose number increases as $\ln t_w$ [1] can equilibrate at T_w. This changes the local field. On resuming cooling particles whose blocking temperature is $\leq T_w$ will again be blocked, but now a small number of particles, whose blocking temperature was greater than T_w will have the equilibrium distribution at T_w, and the susceptibility will be slightly changed. On heating in a small field there will be a small difference in the magnetization. Initially this difference will be negligible because only the smallest particles, that make the least contribution to the moment, will become unblocked at low temperatures. However on further heating larger and more numerous grains become unblocked, and the moment difference increases rapidly until T_w is reached. At this temperature the grains that were responsible for the effect of waiting on the susceptibility begin to be remagnetized, and the moment difference rapidly disappears.

With a mean field theory, the local field H_l is proportional to the local magnetization density, M_l, $H_l = \lambda M_l$. In the present case assemblies of nanoparticles have a range of grain sizes, and $H_l = \lambda \int dV N(V) m_l(V)$, where $N(V)$ is the normalized grain size distribution, and $m_l(V)$ is the orientationally averaged magnetization of a grain whose volume is V .

Consider a subset of particles of volume V , all making an angle θ with H_l, their irregular shape leads to a single easy axis for their magnetiztion; so there are two possible orientations of their magnetic vectors, and the approach to equilibrium is governed by the master equations:

$$\frac{dn^+}{dt} = w^- n^- - w^+ n^+ = n^- \omega e^{-\frac{KV + JH_l V \cos\theta}{T}} - n^+ \omega e^{-\frac{KV - JH_l V \cos\theta}{T}}$$
$$\frac{dn^-}{dt} = w^+ n^+ - w^- n^- = n^+ \omega e^{-\frac{KV - JH_l V \cos\theta}{T}} - n^- \omega e^{-\frac{KV + JH_l V \cos\theta}{T}}$$

where ω is an attempt frequency on the order of 10^8 Hz, K is the anisotropy constant, J is the saturation magnetization, and all energies are in temperature units. Subtracting,

$$\frac{dn^+}{dt} - \frac{dn^-}{dt} = 2\omega e^{-\frac{KV}{T}} \left(n^- e^{-\frac{JH_l V \cos\theta}{T}} - n^+ e^{\frac{JH_l V \cos\theta}{T}} \right)$$

$$= \omega e^{-\frac{KV}{T}} [(n^- e^{-\frac{JH_l V \cos\theta}{T}} - n^+ e^{\frac{JH_l V \cos\theta}{T}}) + (n^- e^{\frac{JH_l V \cos\theta}{T}} - n^+ e^{-\frac{JH_l V \cos\theta}{T}}) +$$
$$(n^- e^{-\frac{JH_l V \cos\theta}{T}} - n^+ e^{\frac{JH_l V \cos\theta}{T}}) - (n^- e^{\frac{JH_l V \cos\theta}{T}} - n^+ e^{-\frac{JH_l V \cos\theta}{T}})]$$
$$= \omega e^{-\frac{KV}{T}} [(n^- - n^+) 2 \cosh \frac{JH_l V \cos\theta}{T} - 2n^- \sinh \frac{JH_l V \cos\theta}{T} - 2n^+ \sinh \frac{JH_l V \cos\theta}{T})]$$

These equations can be rewritten in terms of the fractional magnetization $f = \frac{n^+ - n^-}{n^+ + n^-}$, becoming

$$\frac{df}{dt} = 2\omega e^{-\frac{KV}{T}} \cosh \frac{JVH_l \cos\theta}{T} (\tanh \frac{JVH_l \cos\theta}{T} - f)$$

At equilibrium $f = \tanh \frac{JVH_l \cos\theta}{T}$. At constant temperature the differential equation is easily solved to yield

$$f = f_0 e^{-(2\omega t e^{-\frac{KV}{T}} \cosh \frac{JVH_l \cos\theta}{T})} + \tanh \frac{JVH \cos\theta}{T} [1 - e^{-(2\omega t e^{-\frac{KV}{T}} \cosh \frac{JVH_l \cos\theta}{T})}]$$

f_0 is the value of f at $t = 0$. The result shows that the initial value of f is decaying exponentially with time, and being replaced by the equilibrium value at T. Because of the double exponential, the time dependence is strongly volume dependent, and if $JH_l < K$, or $H_l < H_c$ (the coercive force), to an excellent approximation if $V > \frac{T}{K} \ln \omega t$, $f = f_0$, and if $V < \frac{T}{K} \ln \omega t$, $f = \tanh \frac{JVH \cos\theta}{T}$, and

$$H_l = \lambda \int dV m_l(V) \cong$$
$$\lambda \int_0^{\pi/2} \sin\theta \cos\theta d\theta [\int_0^{\frac{T}{K} \ln \omega t} dV N(V) JV \tanh \frac{JVH_l \cos\theta}{T} + \int_{\frac{T}{K} \ln \omega t}^{V_{\max}} dV N(V) JV f_0]$$

During cooling, starting at a high enough temperature for all the grains to be in equilibrium, they will initially be able to maintain their equilibrium distribution. Eventually, however, the relaxation rate, $\frac{1}{\tau} = \omega e^{-\frac{KV}{T}}$, becomes too slow for this to be possible, and the grains become blocked. The temperature at which this occurs, the blocking temperature, is defined here as that temperature below which a grain flips its magnetization no more than once, thus, if the rate of cooling is $\frac{dT}{dt} = \alpha$, $\alpha \frac{dt}{\tau}$ flips will occur in time dt, and the condition becomes $1 = \int_0^{T_b} \frac{dT}{\alpha} \omega e^{-\frac{KV}{T}} = \frac{\omega}{\alpha} KV [\frac{T_b}{KV} E_2(\frac{KV}{T_b})]$ where $E_2(x)$ is the exponential integral function of order 2. Using the asymptotic expansion of E_2 [12], $\frac{\omega}{\alpha} \frac{T^2}{KV_T} e^{-\frac{KV}{T_b}} \cong 1$, and $\frac{KV}{T_b} + \ln \frac{KV}{T_b} \cong \ln \frac{\omega}{\alpha} T_b$, $\omega \tilde{} 10^8$ Hz; so the value of T_b does not have much effect on the right hand side. Replacing $\frac{T_b}{\alpha}$ by a suitable average for the time it takes to cool the sample from T_b to a low temperature, $\frac{KV_b}{T_b} + \ln \frac{KV_b}{T_b} \tilde{} 23$, and $\frac{KV_b}{T_b} \tilde{} 20$.

During cooling the magnetization at a temperature T contains the sum of the magnetizations of all grains whose blocking temperature is less than T, $JV \tanh \frac{JVH_l \cos\theta}{T}$, plus the magnetizations of all the blocked grains, letting $x = \cos\theta$:

$$H_l \cong \lambda \int_0^1 x dx [\int_0^{V_b(T)} dV N(V) JV \tanh \frac{JVH_l(T)x}{T} + \int_{V_b(T)}^{V_{\max}} dV N(V) JV \tanh \frac{20JVH_l(T_b)x}{T_b(V)}]$$

If the sample has cooled to a temperature that is low enough for all the grains to be blocked,

$$H_l \cong \lambda \int_0^1 x dx \int_0^{V_{\max}} dV N(V) JV \tanh \frac{20JH_l(\frac{KV}{20})x}{K}$$

If a small field, h, is now applied at an angle ϕ to the grains, and the sample heated to a temperature T, all grains whose blocking temperature is less than T will have the equilibrium distribution corresponding to T. The magnetization will be

$$M_l \cong \int_0^1 x dx \{ \int_0^{V_b(T)} dV N(V) JV \tanh \frac{JV[H_l(T)x + h\cos\phi]}{T} + \int_{V_b(T)}^{V_{\max}} dV N(V) JV \tanh \frac{20JH_l(\frac{KV}{20})x}{K}]$$

The local field is λM_l; so heating results in a field equal to

$$H_h \cong H_l + \int_0^1 x dx \{ \int_0^{V_b(T)} dV N(V) JV [\tanh \frac{JV(H_l x + h\cos\phi)}{T} - \tanh \frac{JVH_l x}{T_b(V)}].$$

If T is low, $V_b(T) << V_{\max}$, the integral is small and the correction to H_l can be neglected, and $H_h \approx H_l$. This will be done in the following treatment.

Somewhere in the sample a region exists that is identical except that the interaction field has the opposite sign:

$$M_l^- \cong \int_0^1 x dx \{ \int_0^{V_b(T)} dV N(V) JV \tanh \frac{JV[-H_l x + h\cos\phi]}{T} - \int_{V_b(T)}^{V_{\max}} dV N(V) JV \tanh \frac{20JH_l x}{K}]$$

Summing, and taking advantage of the smallness of h,

$$M \cong \frac{h\cos\phi}{T} \int_0^1 x dx \int_0^{V_b(T)} dV N(V) (JV)^2 \cosh^{-2} \frac{JVH_l x}{T}$$

If the cooling is interrupted for a time t_w at a temperature T_w, H_l becomes

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$$H_{l,w} \cong \lambda \int_0^1 x dx [\int_0^{\frac{20T_w}{K}} dV N(V) JV \tanh \frac{20JH_{l,w}x}{K} +$$
$$\int_{\frac{20T_w}{K}}^{\frac{T_w}{K}\ln \omega t_w} dV N(V) JV \tanh \frac{JVH_{l,w}x}{T_w} + \int_{\frac{T_w}{K}\ln \omega t_w}^{V_{\max}} dV N(V) JV \tanh \frac{20JH_{l,w}x}{K}]$$
$$= H_l + \Delta H = H_l + \lambda \int_0^1 x dx [\int_{\frac{20T_w}{K}}^{\frac{T_w}{K}\ln \omega t_w} dV N(V) JV (\tanh \frac{JVH_{l,w}x}{T_w} - \tanh \frac{JVH_lx}{T_b(V)})]$$

and the moment produced on heating is

$$M_w \cong \frac{h\cos\phi}{T} \int_0^1 x dx \int_0^{V_b(T)} dV N(V)(JV)^2 [1 - \tanh^2 \frac{JV(H_l+\Delta H)x}{T}]$$

ΔH is clearly small; so

$$\Delta M = M_w - M \cong$$
$$-2\frac{J^3}{T^3} h\cos\phi \int_0^1 x^2 dx \int_0^{V_b(T)} V^3 dV N(V)[\tanh \frac{JVH_lx}{T} \cosh^{-2} \frac{JVH_lx}{T}]\Delta H$$

The quantity $\tanh \frac{JVH_lx}{T} \cosh^{-2} \frac{JVH_lx}{T}$ reaches a maximum at $\frac{JVH_lx}{T} \approx 0.6$, and drops to about 10% of its maximum when $\frac{JVH_lx}{T} \approx 1.5$. Therefore it can be concluded that if the local field becomes very large the effect of waiting will disappear, and the spin glass is replaced by a magnetic glass. In this connection no ageing effects at all were observed in two different concentrated assemblies of cobalt particles, one with a mean size of 3 nm, the other with a mean size of 8 nm [13]. The samples were prepared by evaporating the liquid from a colloidal suspension to dryness; so the individual particles were separated by the thickness of a 2nm polymer layer. In both cases the shift in the position of the peak in the ZFC magnetization was substantial, with the temperature of the peak more than doubling, suggesting that the local field was on the order of the coercive force.

Bearing the above considerations in mind the remaining analysis assumes $\frac{JVH_lx}{T} < 1$, in which case,

$$\Delta M \approx -\frac{J^4 H_l}{6T^4} h \Delta H \int_0^{V_b(T)} V^4 dV N(V)$$

$N(V)$ is usually approximated by a log-normal distribution: $N(V) \approx \frac{e^{-\frac{\ln V - \ln V_m}{2\sigma^2}}}{V}$ where σ is the standard deviation, and V_m is the most probable volume; so, letting $b = \sqrt{2}\sigma$, and $\frac{V}{V_m} = x$

$$\Delta M = -\frac{hH_l\Delta H}{6}\left(\frac{JV_m}{T}\right)^4 \int_0^{\frac{T}{KV_m}\ln\frac{\omega T}{20\beta}} x^3 dx e^{-\frac{1}{b^2}\ln^2 x}$$

Now $KV_m\tilde{\ }20T_m$ where T_m is the temperature of the peak in the ZFC

magnetization curve for a dilute *non-interacting* sample; so

$$\Delta M = -\frac{hH_l\Delta H}{6}\left(\frac{JV_m}{T}\right)^4 \int_{-\infty}^{\ln\frac{T}{T_m}} e^{3y}e^{-\frac{y^2}{b^2}} =$$
$$-\frac{\sqrt{\pi}hH_l\Delta H}{12}\left(\frac{JV_m}{T}\right)^4 e^{\frac{3b^2}{4}}\left[1 + \operatorname{erf}\left(\frac{\ln\frac{T}{T_m}-\frac{3b^2}{2}}{b}\right)\right]$$

letting $\gamma = \frac{T_w}{T_m}, y = \frac{T}{T_w}$, ΔM can be rewritten as $\Delta M \approx \frac{const.}{y^4}\operatorname{erf}c(\frac{3}{2}b - \frac{\ln\gamma y}{b})$

The resulting temperature dependence is very strong, and the magnitude of ΔM increases rapidly with temperature. This is illustrated in the figure below. However when the temperature exceeds T_w the effect of waiting begins to be removed, since the grains affected by the delay are now having their moments reset. If ΔH_0 is the value for $T < T_w$, when $T > T_w$

$$\Delta H \simeq \Delta H_0 \frac{\int_{\frac{T}{T_m}}^{\frac{aT_w}{T_m}} xdxe^{-\frac{1}{\sigma^2}\ln^2 x}(\frac{1}{T}-\frac{1}{T_m x})}{\int_{\frac{T_w}{T_m}}^{\frac{aT_w}{T_m}} xdxe^{-\frac{1}{\sigma^2}\ln^2 x}(\frac{1}{T_w}-\frac{1}{T_m x})} =$$

$$\Delta H_0 \frac{\frac{1}{y}[\operatorname{erf}(\frac{\ln a\gamma-\sigma^2}{\sigma})-\operatorname{erf}(\frac{\ln\gamma y-\sigma^2}{\sigma})]-\gamma e^{-\frac{3\sigma^2}{4}}[\operatorname{erf}(\frac{\ln a\gamma-\frac{\sigma^2}{4}}{\sigma})-\operatorname{erf}(\frac{\ln\gamma y-\frac{\sigma^2}{4}}{\sigma})]}{[\operatorname{erf}(\frac{\ln a\gamma-\sigma^2}{\sigma})-\operatorname{erf}(\frac{\ln\gamma-\sigma^2}{\sigma})]-\gamma e^{-\frac{3\sigma^2}{4}}[\operatorname{erf}(\frac{\ln a\gamma-\frac{\sigma^2}{4}}{\sigma})-\operatorname{erf}(\frac{\ln\gamma-\frac{\sigma^2}{4}}{\sigma})]}$$

and ΔH, hence ΔM rapidly disappear at temperatures above T_w. ΔM is plotted in the figure.

Considering the limitations of a mean field approach the agreement between theory and experiment is excellent. The failure to reproduce the rounded transition from decreasing to increasing ΔM at T_w can be traced to the initial assumption that grains block abruptly at the blocking temperature.

The strong dependence of the effect on the width of the grain size distribution is interesting, but not surprising: rejuvenation is due to the interaction field frozen in by the grains blocked on cooling. Waiting allows grains that were blocked during cooling to T_w to reach their equilibrium distribution at T_w, and the wider the grain size distribution the wider will be the temperature range over which the grains grains block. "Rejuvenation" is just the gradual replacement of the interaction field frozen in during waiting by the equilibrium field during heating; so, the wider the distribution, the larger the number of smaller grains that will reach their equilibrium distribution during waiting, and become blocked on cooling.

It has been shown that a straight forward mean field theory can account for rejuvenation in superspin glasses. In contrast to other approaches no droplets are assumed to exist, nor is a hierarchy of energy levels invoked, and while a

chaotic distribution of spins is consistent with the theory, no aspects of chaos theory are employed.

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Figure 1: the difference in moment introduced on heating between two samples cooled in zero field in which one was held at an intermediate temperature normalized to the difference in the moment at the waiting temperature plotted against the temperature normalized to the waiting temperature. The three curves on the left of the figure are computed for 3 different values of the standard deviation in a log-normal particle size distribution. The value of the standard deviation had negligible effect on the curve on the right of the figure. The open circles are experimental data taken from Sasaki et al. [11].

Figure 1:

This figure "image002.png" is available in "png" format from:

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